REPORT

Studies on enhancing transverse thermal conductivity in carbon/carbon composites

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14. ABSTRACT
In the present studies, attempts were made to prepare multi-walled carbon nanotubes (MWNTs) on a large scale in the form of aligned carbon nanotubes as arrays. Arrays of these carbon nanotubes were densified, like in carbon felt densification process by filling the space within the nanotubes. Therefore, the work undertaken in the present studies was to develop arrays of MWNTs and to develop aligned MWNTs composite films using chemical vapor infiltration technique. Substantial characterization was completed and documented. Thermal conductivity of as purified aligned carbon nanotube film was 7.169 W/m.K. After infiltration, this densified film showed thermal conductivity of about 16.0 W/m.K. The lattice defects present in these nanocomposites were minimized by graphitization at high temperature. The heat treatment of these films at 2400?C yielded increase in thermal conductivity to 10.2761 and 51.319 W/m.K for 950 ?C and 1050 ?C infiltrated films, respectively.

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Carbon nanotubes have a wide range of unexplored potential applications in various technological areas such as highly adsorbing or highly conducting materials. Eversince the discovery of carbon nanotubes (CNT) and the realization of their unique properties, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit extraordinary properties. Similarly, CNT possess one of the highest thermal conductivities known, which suggests their use in composites for thermal management.

To date, development of nanotubes based product has been delayed owing to lack of availability carbon nanotubes in large quantities and lack of control of their growth. Among the three methods to produce CNTs, catalytic chemical vapor deposition methods promise to be simple, more controllable and suitable for large-scale production at low cost. The growth process involves heating a catalyst material to high temperature in tube furnace and flowing a hydrocarbon gas through the tube reactor over a period of time. Materials grown over the catalyst are collected upon cooling the system at room temperature. Therefore in the present studies, attempts were made to prepare multi walled carbon nanotubes (MWNTs) on a large scale in the form of aligned carbon nanotubes as arrays. Arrays of these carbon nanotubes were densified like in carbon felt densification process by filling the space within the nanotubes. Therefore, the work undertaken in the present studies was to develop arrays of multiwalled carbon nanotubes (MWNTs) and to develop aligned MWNTs composite films using chemical vapor infiltration technique.

Scanning electron microscope (SEM-Hitachi S-3000N), transmission electron microscope (TEM -Philips, Tecnai-20) and high resolution transmission electron microscope (HRTEM) were used to analyze microstructure of CNTs and nanocomposites. The thermal stability and extent of purification of nanotubes was checked using thermo gravimetric analysis (Mettler TG 50) in air atmosphere. XRD of the nanocomposites was carried out using X-Ray Diffractometer Philips, X'pert model. Raman spectroscopy (Renishaw InVia Raman microscope) was used to evaluate the structure and crystallinity of CNTs and their composites. Measurements of thermal diffusivity of these nanocomposites were carried out from room temperature to 300 °C by laser flash method on NEITZSCH Micro flash- 300.

Hydrogen gas has been observed to play crucial role in the growth of filamentous carbon deposition in CVD method. Analysis showed the diameter of carbon nanotubes to vary from 50 – 100 nm and the length of these randomly oriented CNTs is up to several micrometers with negligible (~2 weight %) metal impurities after purification. The Films of aligned carbon nanotubes were synthesized by decomposition of catalyst-hydrocarbon solution on quartz glass plates of 1 square inch area in horizontally arranged quartz tube reactor. The areas of the prepared film were 1 square inch and were up to 2 mm in height (thickness). The purification of films deposited on quartz substrate was carried out by treatment with HNO_3 solution at 50 to 60 ^oC for 50 hours without destroying the arrays of integrity. The growth of nanotubes on PAN based carbon fiber was also carried out using ferrocene-xylene system. This study was carried out because the use of these types of hybrid reinforcement (carbon nanotubes coated carbon fiber) may improve the mechanical and thermal properties of nanocomposites as compared to conventional composites.

Raman spectra were taken from the top surface of vertically aligned CNTs film after purification. The sharp G band at ~1581 cm^{-1} reveals the existence of more graphitic sheets than disorder carbon present in the ACNTs film. The relative intensity (I_D/I_G) of the sample is 0.67, which is low. This confirms to well-ordered structure of CNTs. The higher synthesis temperature and catalyst concentration leads to formation of larger size catalytic particles which gives the nanotubes with larger diameter and same time these affect the alignment of CNTs on the substrate. The bulk density of purified aligned carbon nanotubes films varies from 0.30 - 0.40 gm/cm^3.

Aligned carbon nanotubes films synthesized by chemical vapor deposition method are very fluffy and had not much strength even for handling. Densification of these films was performed by filling the space between the CNTs through deposition of the pyrocarbon on at 950-1000°C. SEM studies showed that the film was well infiltrated using methane. The density of film increased from 0.4 gm/cm^3 of as purified ACNTs film to 1.4 gm/cm^3. The effect of methane gas concentration, gas flow of methane-argon gas mixture, infiltration temperature and infiltration time on the microstructure of analysis carbon deposits have been studied. SEM study of composite film prepared with the lower gas flow (25 cc/min) of methane-argon gas mixture (1:4 gas flow ratio) shows very low quality of pyrocarbon and other carbon impurities in the particulate form (soot like) and have no smooth microstructure. The experiment carried out with higher gas flow (125 cc/min) of methane-argon gas mixture (1:4 gas flow ratio) shows a continuous and uniform thickening of primary nanotubes due to shorter residence time of carbon species in the reaction zone as compared to lower gas flow rates. CNTs were found to be uniformly covered by CVI deposited pyrolytic carbon; hence the diameter of CNTs increases from 20-60 nm to 400-500 nm. The intimately packed CNTs were seen to be more infiltrated by filling tiny space as compared to other large space. This is because carbon species present in the gases are easily trapped into narrow gap. The density of ACNTs composite changed from 0.40 gm/cm^3 of as purified film to 1.4 gm/cm^3 by densification process, which is about four times larger than pristine nanotubes. The infiltration of film at 1050 °C shows the well order thickening of nanotubes as compare to the result obtained with 950 °C. The structure of pyrocarbons was studied by Raman analysis. The I_D/I_G ratio observed were ~ 0.8 and ~0.67 for 950 °C and 1050 °C synthesized pyrolytic carbon respectively. These ratios reveal the more graphitic nature of pyrolytic carbon. The nature of carbon deposited on CNTs was studied by Raman measurement and it shows broader D band at ~1357 cm^{-1} and quite sharper G band at ~1599 cm^{-1}. Thermal conductivity of as purified aligned carbon nanotube film is 7.169 W/m.K. After infiltration, this densified film shows thermal conductivity of about 16.0 W/m.K. The lattice defects present in these nanocomposites were minimized by graphitization at high temperature. The heat treatment of these films at 2400°C shows increase in thermal conductivity to 10.2761 and 51.319 W/m.K for 950 °C and 1050 °C infiltrate films respectively.